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COMPLETE SPECIFICATION

Method for Clarifying Water

We, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of 5 Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the 10 following statement:—

This invention relates to the clarification of water and is particularly directed to a method for facilitating the removal 15 of finely divided suspended solids from water.

In the treatment of water for industrial or municipal use, particularly where surface waters such as those from lakes 20 and rivers are used, it is frequently necessary to remove finely divided solids such as silt and clay in order to produce water sufficiently clarified for the desired use. Similar problems are encountered 25 where it is desired to clarify for reuse industrial process water contaminated with finely divided solids. Removal of such finely divided solids by filtration alone has generally proved impracticable 30 in large scale operations.

It has been common practice for many years to employ coagulants, such as aluminium sulphate and iron chloride, to facilitate removal of suspended solids by 35 sedimentation or filtration. Such agents usually form a gelatinous and voluminous floc which enmeshes the finely divided solid matter and thereby facilitates subsequent removal of such solids by sedimentation or filtration. However, certain 40 difficulties are encountered in the use of such coagulants. Thus, for example, special flocculation equipment is usually required for building the floc to the 45 proper size and large sedimentation

vessels are required to separate the relatively slow-settling floc from the clarified water. In some cases, excessive amounts of the coagulant are required to achieve the desired degree of clarification. 50

It is an object of the present invention to provide an improved method for clarifying water. It is a further object to provide an improved method for clarifying water with coagulants whereby less of 55 such agent is required for producing water of the desired clarity.

It has now been discovered that the incorporation of a water-soluble acrylamide polymer in water treated with a 60 coagulant accomplishes the formation of a rapidly settling floc and thereby facilitates the separation of finely divided suspended solids from such water. It is among the advantages of the invention 65 that less coagulant is needed for a given degree of clarification when such acrylamide polymers are used. It is a further advantage of the invention that the desirable results are accomplished with 70 only very small amounts of the acrylamide polymer.

According to the present invention there is provided a method for clarifying water which comprises the steps of admix- 75 ing with the water a coagulant and an acrylamide polymer.

The term "coagulant" refers to an iron or aluminium compound selected from ferrous sulphate, ferric chloride, chlorin- 80 ated ferrous sulphate, sodium aluminate, aluminium sulphate or aluminium chloride.

The acrylamide polymers effective in the invention are water-soluble and 85 characterized by a minimum of cross linking between polymer chains. Effective polymers are those having viscosities of at least about 2 centipoises for an aqueous 0.5 per cent by weight solution thereof in 90

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distilled water adjusted to a pH of 3 to 3.5 and at a temperature of 25°C. as determined with an Ostwald viscosimeter. The term "viscosity" as employed in the following description and claims refers to the viscosity of an aqueous 0.5 per cent by weight solution under the conditions set forth above. The term "acrylamide polymer" includes both the homopolymer of acrylamide and copolymers of acrylamide with up to about 15 mole per cent of other monomers such as acrylic and methacrylic acids and their lower alkyl esters, containing not more than 4 carbon atoms in the alkyl group, acrylonitrile, methacrylonitrile, methacrylamide, vinyl alkyl ethers, styrene, vinyl chloride and vinylidene chloride, each such copolymer being characterized by water-solubility, low degree of cross linking and viscosity properties as set forth above.

Water-soluble acrylamide polymers are sometimes characterized by a greater or less degree of hydrolysis, that is, contain some free carboxyl groups. This condition is dependent upon the method of manufacture of the polymer, the presence or absence of small amounts of acrylic acid in the starting monomer and conditions of storage of the polymer. The polymer products appear to be equivalent whether the carboxyl groups result from copolymerization of acrylamide with acrylic acid or from hydrolysis of amide groups subsequent to polymerization. In the practice of the present invention, the operable acrylamide polymers include those having not more than about 15 per cent of the amide groups replaced by carboxyl groups.

In carrying out the invention, the coagulant and acrylamide polymer are added to the raw water to be clarified in any suitable fashion, provided that rapid and thorough mixing of the coagulant and the polymer throughout the mass of water is accomplished. In general, the coagulant is added either as a solid or an aqueous solution by the conventional methods of water treating practice. The acrylamide polymer is added as an aqueous solution or as a finely divided powder. The addition of the polymer in the form of an aqueous solution constitutes a preferred mode of operation.

In operations where the acrylamide polymer is added in finely divided form it is essential that the powdered polymer be added to the raw water portionwise with vigorous agitation to assure the complete solution of the polymer without the formation of jelly-like masses which dissolve only slowly. In general, it is preferred to employ polymer ground to pass a screen of 200 meshes per inch. To

facilitate grinding and distribution, it is frequently desirable to incorporate a finely divided inert carrier with the polymer powder.

Suitable finely divided inert carriers include diatomaceous earth, various clays, pyrophyllite and talc. In such compositions comprising an acrylamide polymer and finely divided inert carrier, the acrylamide polymer may conveniently comprise from about 10 to 95 per cent by weight of the finished composition.

In operations employing an aqueous solution of acrylamide polymer it is generally convenient to dissolve the acrylamide polymer with vigorous agitation to prepare an aqueous stock solution containing from about 0.5 to 5 per cent by weight of polymer. The exact concentration of polymer in the stock solution will vary depending upon the viscosity of the particular polymer. Thus, for example, with acrylamide polymer having viscosities of from about 2 to 5 centipoises, it is preferred to prepare stock solutions containing from about 1 to 5 per cent by weight of polymer. With polymers of higher viscosity, it is generally desirable to employ solutions containing not more than about 2 per cent by weight of polymer. Such stock solutions may be added directly through suitable proportioning or metering equipment into the water to be clarified. The stock solution may be diluted further to prepare a treating solution. Such dilute treating solutions have the advantage of being readily introduced in conventional liquid chemical feeders while maintaining accurate dosage at the low levels employed in the invention. In practice, such treating solutions advantageously contain not more than about 0.5 per cent by weight of acrylamide polymer and, in general, treating solutions containing from about 0.01 to about 0.1 per cent by weight of polymer are preferred.

The exact amounts of coagulant and acrylamide polymer to be employed will vary depending upon such factors as the total amount of suspended solids to be flocculated, the nature of such solids, the pH of the water and the concentration of dissolved electrolytes in the particular water. The most economical amounts of reagents to be employed with a given water supply and any required adjustment of pH can be determined in each instance by jar tests in accordance with standard waterworks practice, as set forth, for example, on page 36 *et seq.* of E. S. Hopkins' *Water Purification Control*, Third Edition, The Williams and Wilkins Co., Baltimore, 1948. In any case, sufficient of the acrylamide

polymer is employed to accomplish the formation of a readily settleable floc and to facilitate the separation of the finely divided solids. In practice, it has been found that the amount of acrylamide polymer required is somewhat dependent upon the viscosity of the polymer employed and such amount is roughly inversely proportional to the viscosity as defined above. In general, from about 0.02 to about 5 parts by weight of acrylamide polymer and from about 3 to about 200 or more parts by weight of coagulant are employed per million parts by weight of water to be clarified, although larger amounts may sometimes be required in special circumstances.

Following is a description by way of example of methods of carrying the invention into effect.

EXAMPLE 1

A commercial water clarification installation for producing boiler feed water from river water required a dosage of 100 to 120 parts by weight of alum and 50 to 60 parts by weight of sodium silicate per million parts by weight of water to produce clarified water at the rate of 200 gallons per minute. Attempts to increase the rate of throughput at this dosage resulted in carry-over of floc in the effluent overflow from the sedimentation vessel.

A clarification operation was carried out on the above raw river water in the aforementioned equipment using a dosage of 40 parts by weight of alum and 0.5 parts by weight of a homopolymer of acrylamide, characterized by a viscosity of 9 centipoises and hydrolysis of 4.1 per cent, per million parts by weight of water. The alum was added in the form of an aqueous solution of hydrated aluminium sulphate and the acrylamide polymer in the form of a dilute aqueous solution containing 0.025 per cent by weight of the polymer. This treatment was found to produce a floc which settled very rapidly so that over 500 gallons of clarified water per minute could be produced while maintaining the floc blanket well below the overflow from the sedimentation vessel.

EXAMPLE 2

River water containing suspended finely-divided solids equivalent to 250 parts of silica on the American Public Health Association scale per million parts of water, was mixed with 25 parts by weight of alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 14.5 \text{ H}_2\text{O}$) per million parts by weight of water. The alum was added in the form of an aqueous solution containing 10 grams of alum per litre and the mixing of the alum and water was accomplished rapidly with a high speed propeller agitator. Thereafter

the treated water was transferred to a vessel equipped with small paddle agitators operating at 40 revolutions per minute. This slow speed agitation was continued for 15 minutes and then discontinued to allow sedimentation to occur. After two minutes settling a sample was withdrawn from two inches below the water surface and the turbidity thereof determined with a Klett-75 Summerson photoelectric colorimeter.

Similar determinations were carried out employing portions of the same raw water treated with 25 parts of alum in the above manner and with varying amounts of a homopolymer of acrylamide per million parts of water. The acrylamide polymer was characterized by a viscosity of 9.8 centipoises and hydrolysis of 4 per cent and was added as an aqueous solution containing 0.05 per cent by weight of polymer. The results obtained are summarized in the following table wherein the turbidities are expressed as parts per million of silica on the American Public Health Association scale. (*Standard Methods for the Examination of Water and Sewage*, Ninth Edition, American Public Health Association, New York, 1946, pages 12 to 14). The colorimeter readings were converted to said scale using a calibration curve derived by comparison with a Hellige turbidimeter [A. A. Hirsch, *Water and Sewage Works*, 93, 84-5 (1946)].

Acrylamide		Turbidity	
Alum, parts per million	Polymer, parts per million		
25	0	5	105
25	0.125	1.3	
25	0.250	0.8	

EXAMPLE 3

Further determinations were carried out employing the method, reagents and river water of Example 2 with the use of a 2 hour period of stirring with the paddle agitators. The observed turbidities at 2 inch depth, determined as in Example 2, after 2 minutes from the initiation of settling, are recorded in the following table:

Acrylamide		Turbidity	
Alum, parts per million	Polymer, parts per million		
25	0	20	120
12.5	0.125	1.6	

EXAMPLE 4

Raw river water having a turbidity of about 200 parts of silica per million was mixed with an aqueous 1 per cent by weight solution of ferric chloride to provide 25 parts by weight of ferric chloride per million parts by weight of water. Into the resulting mixture, sodium hydroxide was added in dilute aqueous

solution to adjust the mixture to a pH of 6. A portion of the above described mixture was stirred for a period of 20 minutes with small paddle agitators operating at 40 revolutions per minute. At the end of this time, the agitators were stopped to allow sedimentation to occur. After 2 minutes of settling a sample was withdrawn from a depth of 2 inches below the surface of the water and the turbidity thereof determined as in Example 2.

To further portions of the ferric chloride-water mixture varying amounts of a homopolymer of acrylamide, characterized by a viscosity of 9.8 centipoises and hydrolysis of 4 per cent, were added. The polymer was added in the form of an aqueous 0.04 per cent by weight solution and the resulting mixture stirred for 20 minutes as set forth above. Thereafter, sedimentation was initiated and samples withdrawn for turbidity determinations as in Example 2. The results are summarized in the following table, wherein turbidities are recorded in terms of parts per million of silica as in the preceding examples:

	Ferric Chloride, parts per million	Acrylamide Polymer, parts per million	Turbidity
30	25	0	8
	25	0.25	3
	25	0.15	3
	25	0.10	3
35	25	0.05	3
	25	0.025	4

EXAMPLE 5

In the recovery of foundry sand by washing, the overflow from cone classifiers, which remove the heavier sand, constitutes a difficultly settleable slime. The suspended solids in this slime, comprising chiefly fine coal and clay, settle very slowly so that after the suspension has been held for several days in a large area sedimentation pond, the effluent upper layer still contains 1 to 2 per cent by weight of solids and is very dark and turbid. A portion of such turbid effluent is treated with aluminium sulphate at the rate of about three parts by weight per million parts by weight of water and with a homopolymer of acrylamide, characterized by a viscosity of 7.5 centipoises and hydrolysis of 5 per cent, at the rate of 0.05 parts by weight of acrylamide polymer per million parts by weight of water. The finely divided solids flocculate quickly to produce a rapid settling floc and to provide a clear supernatant water layer after a short sedimentation period.

EXAMPLE 6

Ferric sulphate was employed as the coagulant for removing suspended solids from brine from the Arbuckle shale

formation in Oklahoma to produce clarified brine for use in the waterflooding technique of secondary oil recovery. The brine was mixed with 40 parts by weight of ferric sulphate per million parts of brine and sufficient lime to give a final pH of 9. This treatment was carried out in commercial clarifying equipment and produced a lightfloc which settled relatively slowly so that some suspended solids were carried over in the effluent water.

The feed to the above clarifying equipment was modified to introduce 24 parts by weight of ferric sulphate and 0.16 parts by weight of a homopolymer of 80 acrylamide per million parts of the brine. Sufficient lime was introduced to adjust the brine to a pH of 9 as before. The acrylamide polymer employed was characterized by a viscosity of about 8 centipoises and was added in the form of a dilute aqueous solution containing 0.1 per cent of the polymer. This treatment produced a floc which was larger and denser than that produced with the 40 parts per million of ferric sulphate. The floc settled rapidly to produce water of improved clarity as compared with that previously produced.

In similar operations employing ferric chloride in treating oil field waste brine and aluminium sulphate in treating recycle water for secondary oil recovery by waterflooding, the incorporation of acrylamide polymers, characterized by viscosities of from 6 to 16 centipoises, in the treated brine or water at dosages of from 0.1 to 0.2 parts by weight per million parts of brine or water results in the formation of excellent flocs whereby finely divided solids are readily separated to produce clarified brine or water.

WHAT WE CLAIM IS:—

1. A method for clarifying water which comprises the steps of admixing with the water a coagulant and an acrylamide polymer.
2. A method for facilitating the separation of finely divided suspended solids from water which comprises adding to said water a coagulant from the group consisting of iron and aluminium coagulants and a sufficient amount at least 0.02 parts by weight per million parts by weight of water of an acrylamide polymer to accomplish the formation of a readily settleable floc.
3. A method as claimed in Claim 1 or Claim 2 wherein the acrylamide polymer is added in the form of a dilute aqueous solution.
4. A method for clarifying water as claimed in any one of the preceding claims which method comprises the steps of admixing with said water from 3 to 200

parts by weight of a coagulant and from 0.02 to 5 parts by weight of an acrylamide polymer per million parts by weight of water.

- 5 5. A method as claimed in Claim 4 wherein the acrylamide polymer is characterized by a viscosity of at least 2 centipoises for a 0.5 per cent by weight solution thereof in distilled water
- 10 adjusted to a pH of 3 to 3.5 and a temperature of 25°C. as determined with an Ostwald viscosimeter.

6. A method for clarifying water

according to Claim 1 substantially as described in any one of the specific examples hereinbefore set forth.

7. Water when clarified by the method claimed in any one of the preceding claims.

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